

Technical Status Report No. 9

Chemistry of Planetary Atmospheres and Comets

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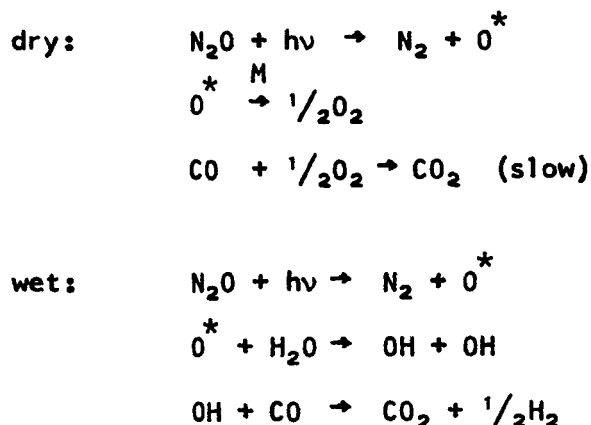
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Carbon Monoxide Oxidations

Further studies of CO oxidation using the iodine lamp have been in progress. Using the 2062 line, N₂O was dissociated in the presence of CO. Considerable oxygen is formed when the system is dry, but with moisture present an entirely different series of reactions occurs which rapidly oxidizes the CO. Even oxygen added to the (wet) system prior to irradiation is consumed, although only the N₂O can absorb the 2062 radiation.

The results of this work will be presented as part of a presentation to the ACS at the September meeting in Chicago. A copy of the abstract is appended.

The results to date could be explained by the following overall reactions:

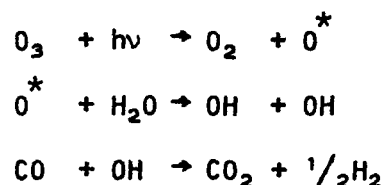


These mechanisms are not totally correct. The formation of NO and N in initial photolysis is minor and ignored here. In addition, the

* The total mechanisms must include O₃ or NO₂ for the consumption of O-atoms and formation of oxygen.

formation of formaldehyde would be expected with H-atoms and CO; this is not readily observed. The hydrogen is found as simply molecular hydrogen.

In the atmosphere of a planet, the oxidation process by such a mechanism could be anticipated with initial photolysis of ozone, for example:



Therefore this work seems to have particular importance for atmospheric chemistry, since this additional source of OH radicals may have many ramifications which have not been fully considered.

Isotopic Enrichment Using the Bromine Lamp

The studies of NO photolysis with the 1633 line of bromine have continued. The isotopic enrichment of the N_2 product in $\text{N}^{14}\text{N}^{15}$ was very pronounced. This implies an excitation of the N^{15}O preferentially over N^{14}O . Analysis of the problem suggested that it was possible that the minor constituent (N^{15}O) would be preferentially excited due only to the fact that it was the minor constituent. This was tested by using N^{15}O with only a minor fraction of N^{14}O . The prediction was at least in part verified as the N^{14}O was now preferentially excited although the degree of enhancement or enrichment was slightly less than for the first case.

These results can be interpreted assuming the absorption lines do not entirely overlap each other and attenuation of the radiation varies with the isotopic concentrations. From the geochemical standpoint it is interesting to realize that photochemical separation may occur to a certain extent in the atmosphere; a problem on which we will elaborate soon.

Further details will be presented later at a meeting in Munich on photochemistry. The Abstract will be sent to NASA shortly.

Studies are also continuing in photodetachment of particles by photons. It is now feasible for us to conveniently use liquid helium in a series of experiments at low temperature. This will permit extensive detailed results to be obtained with reasonable effort. The initial work was submitted earlier as an abstract for "The Symposium on Interstellar Grains" and an additional report should be prepared in the near future.

The studies of chemiluminescent reactions have continued. The mechanism of the airglow ($\text{NO} + \text{O} \rightarrow \text{NO}_2 + h\nu$) seems to be gathering more general acceptance. The nitrogen afterglow, however, is very complicated but work at very low pressures is continuing along these lines although at a rather low level. A two body inverse predissociation mechanism seems possible in the rarified atmospheres of the planets.

A new bromine lamp was constructed for irradiation of samples from 77°K to 100°C or higher. This will permit a considerable extension of present studies along this line especially applicable for the atmospheres of Jupiter and Saturn.

Summary of Current Activities

1. A paper entitled "Radiation Equilibria Pertinent to Planetary Atmospheres", by P. Harteck, R.R. Reeves, Jr., B.A. Thompson and R.W. Waldron appeared in *Tellus XVIII*, 192 (1966).
2. A paper entitled "Some Comments on the Venus Temperature" by D.C. Applebaum, P. Harteck, R.R. Reeves, Jr. and B.A. Thompson appeared in *J. Geophys. Res* 71, 5541 (1966).
3. A paper was presented at the Spring ACS meeting, (April 1967) in Miami Beach entitled "Isotopic Enrichment in the Ultraviolet Photochemistry of Nitric Oxide" by R.R. Reeves, Jr., C.F. Schmidt, Jr., B.A. Thompson and P. Harteck.

This paper will be submitted to the *J. of Phys. Chem.* to be included in the papers on stable isotopes as suggested by the chairman of the symposium.
4. A paper entitled "A Preliminary Study of the Photochemistry of Propyne with the 2062 Å Iodine Line" by A. Galli, P. Harteck and R.R. Reeves, Jr. has been accepted for publication in the *ACS Journal of Physical Chemistry* and is scheduled to appear in the June 1967 issue.
5. We are scheduled to attend the Gordon-Research Conference on the physics and chemistry of space at Tilton, N.H., July 1967.
6. A paper will be presented at the fall meeting of the ACS (September 1967) in Chicago entitled "Some Specific Photochemical Reactions

in the Atmosphere" by Paul Harteck and Robert R. Reeves, Jr. This paper discusses the oxidation of CO in the atmosphere in connection with photochemical experiments performed in the laboratory using the iodine lamp. (Abstract attached).

7. A paper will be presented by Dr. Harteck at the "International Conference on Photochemistry" at Munich, Germany in September 1967 entitled "Isotopic Enrichment of Nitrogen by Photochemical Decomposition of NO", by P. Harteck, R.R. Reeves and C. Schmidt. It will present our latest results concerning this system. An abstract will be prepared shortly and copies forwarded to NASA.
8. We have accepted an invitation to present a paper at a symposium on photochemistry and radiation chemistry at Natick, Mass. in April 1968 sponsored by the National Academy of Sciences - National Research Council.